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T. Furusawa, K. Saito, M. Sato, N. Suzuki

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The Cycle Use Test of Pt Based Catalyst for the Steam Reforming of Naphthalene/ Benzene as Model Tar Compounds of Biomass Gasification

Takeshi Furusawa, Katsuhiko Saito, Masahide Sato, Noboru Suzuki, Utsunomiya University, Graduate School of Engineering, Japan

1 Introduction

Biomass gasification offers great potential for alleviating global environmental problems because biomass is a carbon neutral resource [1]. Gasification involves partial oxidation of raw material to obtain a mixture of hydrogen, carbon monoxide, water, and small amount of methane and higher hydrocarbons. The product gas also contains variable amounts of ash particles, volatile alkali metals and tar, which is a complex mixture of aromatics [2]. The condensable compounds in tar may cause problems in downstream equipment making catalytic hot gas cleaning a necessary step in gasification system [3-4]. Several research groups had already reported the excellent catalysts applied for removal of tar derived from biomass gasifier [3-6], while other research groups developed new catalyst for steam reforming of tar model compound such as benzene [7], toluene [8], phenol [9], and naphthalene [10-11]. If one considers about test reaction to find out new catalysts for tar removal, steam reforming of naphthalene/ benzene is most suitable test reaction because both benzene and naphthalene are most stable tar compounds and are difficult to decompose [10-11]. In this point of view, steam reforming of naphthalene under ideal reaction condition or simulated gas condition have been studied over Ni-Cr/Al₂O₃-MgO-La₂O₃ [10], pretreated olivine [12], Ni/WO₃/MgO-CaO [13], Nickel-activated candle filter [14], commercial nickel-based catalysts [11, 15], CaO+MgO [16], Ni/dolomite [17], Ni/olivine [18], Ni/Ce_{0.75}Zr_{0.25}MnO₂ [19] and Ni/MgO [20] to develop new catalyst for tar removal. According to these reported papers, the deposition of carbon species on the catalyst and irreversible adsorption of sulfur atoms on metal surface account for the catalyst deactivation, and several research groups tried to find out solutions for these problems. For example, Fujimoto *et al.* [13] had reported that the addition of WO₃ to Ni/MgO-CaO catalyst improved the resistance to sulfur poisoning and coking under simulated gas condition. Moreover, Li *et al.* [21] had reported that oxidation-decomposition-reduction regeneration process can effectively remove the sub-surface sulfur and completely regenerate the sulfur-poisoned Ni catalysts. However, it can be predicted that the improved catalyst also deactivated finally due to mainly carbon deposition when once catalyst used for tar removal. Therefore, we thought that the points for the regenerated method and catalytic performance of regenerated catalyst also should be considered. From this background, deactivated Ni/MgO catalyst was regenerated by mild oxidation treatment, and regenerated catalyst was used for steam reforming of naphthalene/ benzene under ideal reaction condition in our previous research [22]. It was found that Ni/MgO catalyst has tolerance toward only 3 cycle of steam reforming-oxidation treatment. The obtained results motivate us to find another catalyst which shows the excellent

performance for cycle test of steam reforming-regeneration treatment. In present study, Pt-based catalysts were prepared by impregnation method and used for cycle test of steam reforming of naphthalene/benzene - regeneration treatment. Moreover, either hydrogen treatment or mild oxidation treatment was selected as regeneration method, and the effect of regeneration method on the catalytic performances of Pt-based catalysts was also investigated.

2 Experimental

2.1 Preparation of catalyst

Pt-based catalyst was prepared by impregnating MgO (JRC-MGO-4 500A, 28-38 m²/g) or Al₂O₃ (JRC-ALO-1, 200 m²/g) with aqueous solution of H₂PtCl₆·6H₂O (Kanto Chemical Co.) followed by drying at 383 K overnight. The material was then calcined in air at 873 K for 8 h. The amount of Pt loading on the catalyst was controlled to be 1 wt.%. Naphthalene and benzene were purchased from Kanto Chemical Co., and used without further purification. Naphthalene/benzene solution was prepared to be 1:9 for molar ratio of naphthalene and benzene.

2.2 Characterization

The nitrogen adsorption isotherms of samples (0.1 g) before and after reaction were measured using a Nova 1200e (Yuasa Ionics Co.) to calculate the specific surface area based on the BET method. The samples were degassed at 573 K for 1 h before measurement and were conducted for nitrogen adsorption isotherms under N₂ at 77 K.

XRD measurements of samples before and after reaction were performed on a Rigaku powder diffractometer with Cu-K α radiation. The tube voltage was 40 kV, and the current was 40 mA. The XRD diffraction patterns were taken in the 2 θ range of 10-80° at a scan speed of 2 ° min⁻¹. XRF measurements of catalysts were performed using SEA2010 (SEIKO Instruments Inc.) to calculate the amount of Pt loading on the catalysts. The morphology and size of Pt particles on fresh reduced catalyst and used catalyst was observed by TEM (JEOL 2010). Average size of Pt particles on catalyst was calculated by estimating each size of 100 Pt particles corrected from TEM image.

The profile for the oxidation of carbon species on used catalyst was obtained by Temperature Programmed Oxidation with 10 % O₂/He. All deposited carbon species were oxidized to CO or CO₂, and the consumption of O₂ was detected by TCD. A 40 mL min⁻¹ feed of 10 % O₂/He was used for oxidation and the temperature was firstly ramped at 10 K min⁻¹ to 873 K. Until no peak was observed, the temperature of reactor kept at 873 K for a while and time needs for complete oxidation of deposited carbon species at 873 K was measured. The temperature was subsequently heated up at 10 K min⁻¹ to 1273 K to check the existence of additional carbon species on the catalyst.

2.3 Catalytic tests

2.3.1 Steam reforming of naphthalene/benzene

Catalytic tests were conducted using the atmospheric flow experimental system. The catalyst was palletized, crushed and sieved to 0.35-0.5 mm before use and was reduced in H₂/Ar (50 vol%/50 vol%) mixture with heating rate at 10 K min⁻¹ to 1173 K and held at 1173 K for 1 h. After reduction, the catalyst bed was cooled down to 973~1073 K under Ar flow and the feed gases were allowed to pass through the catalyst bed at a gaseous feed rate of 400 mL min⁻¹. Nitrogen was used to carry the naphthalene and benzene vapors into the reactor with heating all pipelines at 473 K; a flow rate of nitrogen was 40 mL min⁻¹ carrying 0.36 g h⁻¹ of naphthalene and 1.98 g h⁻¹ of benzene. The water was pumped at a flow rate of 3.3~9.9 g h⁻¹ in order to achieve a GHSV of 19200 h⁻¹ (residence time; 0.18 s), based on the apparent bulk density of the catalyst bed (0.8 g cm⁻³) for 1 g of catalyst. Water to carbon of naphthalene and benzene molar ratio is 1~3. The effluent gases from the reactor were fed through cotton filter set inside ice-cold trap and CaCl₂ column, connected in series. Un-reacted naphthalene, benzene and H₂O were recovered in the ice-cold trap. The non-condensable gases, which included C₁-C₃ hydrocarbons, carbon monoxide, carbon dioxide, hydrogen, and nitrogen were analyzed by gas chromatography (HP6890 equipped with a TCD detector, molecular sieve 5A column and porapak Q column). After the reaction, the reactants were switched with Ar at the reaction temperature; subsequently the catalyst was cooled down to room temperature and used for further characterization. The catalytic activity for the steam reforming was evaluated by calculating the carbon conversion to gas [%] using the equation described below;

$$\text{Carbon conversion to gas [\%]} = \frac{\text{Total molar of carbon atoms of gas products}}{\text{Total molar of carbon atoms of feed gases (naphthalene + benzene)}} \times 100 [\%] \quad (1)$$

2.3.2 Cycle test of steam reforming and regeneration treatment

After the steam reforming of naphthalene/benzene at 1023~1073 K for 3 h with catalyst, used catalyst was cooled down to 873 K and was oxidized under 10 % O₂+Ar mixture or reduced under 10 % H₂+Ar mixture at same temperature for 40 min. Regenerated catalyst was heated up to 1023~1073 K again and then reactants fed to regenerated catalyst bed to evaluate the catalytic performance as 2nd run. This cycle for the steam reforming and regeneration treatment was defined as a 1 cycle in present paper. The cycle usage tests repeated until the deactivation of catalyst was observed.

3 Results and Discussion

3.1 The effect of reaction temperatures on the catalytic performances

Figure 1 shows the catalytic performances of Pt/Al₂O₃ catalysts for the steam reforming of naphthalene/benzene at various reaction temperatures with S/C=3. The activity of Pt/Al₂O₃ catalyst was gradually decreased from 85 % to 75 % at 1023 K during 30 h reaction due to

carbon deposition which was confirmed by the result of TPO measurement, while this catalyst showed high and stable activity (carbon conv. to gas: 90 %) at 1073 K for 30 h. Moreover, the catalyst showed low catalytic activity at 973 K. From these obtained results, 1023 K was selected as reaction temperature for cycle test in the case of Pt/Al₂O₃.

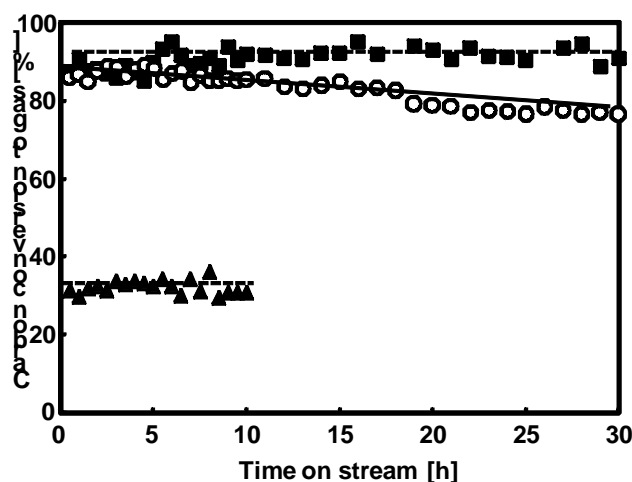


Figure 1: Catalytic performances of Pt/Al₂O₃ catalysts for the steam reforming of naphthalene/benzene at various reaction temperatures with S/C=3: ■ 1073 K, ○ 1023 K, ▲ 973 K.

In the case of Pt/MgO catalyst (not shown here), the activity of Pt/MgO catalyst was remarkably decreased from 80 % to 60 % during initial reaction period (8 h) at 1023 K, while this catalyst showed high and stable activity (carbon conversion to gas: 85 %) for 30 h at 1073 K. Judging from the results, 1023 K was selected as reaction temperature for cycle test with Pt/MgO catalyst as well.

3.2 Cycle tests of Pt-based catalysts

Figure 2 shows the result of cycle test (steam reforming – oxidation treatment) using Pt/Al₂O₃ catalyst at 1023 K with S/C=3. The activity was lost after 1st oxidation treatment, while catalyst showed stable activity during 1st steam reforming step. Since TPO result of oxidized catalyst after 1st oxidation treatment showed no carbeneous species deposited on the catalyst, this observation could be related with changing catalyst structure such as Pt particle size, surface area and crystal structure of support. Among them, there are no differences between fresh catalyst and used catalyst in BET surface area (135 vs. 135 m²/g) and crystal structure (XRD). On the contrary, TEM results indicated that average size of Pt particles on used catalyst significantly increased from less than 3 nm to 5.3 nm. This is probably the reason that Pt/Al₂O₃ catalyst lost its activity after 1st oxidation treatment.

To avoid the aggregation of Pt particles on catalyst, hydrogen treatment was selected as regeneration method instead of mild oxidation treatment. When used catalyst was reduced by hydrogen treatment, the activity of regenerated catalyst was recovered to initial activity of fresh catalyst, and Pt/Al₂O₃ catalyst had tolerance toward 5th cycle test of steam reforming-hydrogen treatment (not shown here). Judging from these results, hydrogen treatment was

suitable regeneration method in the case of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Moreover, Pt/MgO catalyst also lost its activity after 2nd oxidation treatment (not shown here) during cycle test of steam reforming-oxidation treatment. This result could be also explained by the sintering behavior of Pt particles during cycle test.

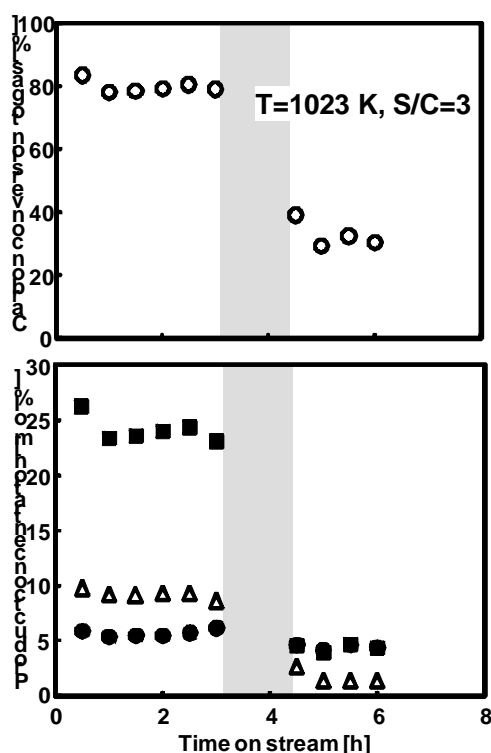


Figure 2: Cycle test of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst at 1023 K with $\text{S}/\text{C}=3$: period for mild oxidation treatment, \blacksquare H_2 , \triangle CO_2 , \bullet CO .

4 Summary

Although $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst showed high and stable activity (carbon conversion to gas: 90 %) for steam reforming of naphthalene/benzene at 1073 K with $\text{S}/\text{C}=3$, this catalyst gradually lost its activity at 1023 K with $\text{S}/\text{C}=3$ due to deposition of carbeneous species. Two kinds of regeneration treatment was conducted to enlong the life time of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Although regeneration treatment completely remove the carbeneous species from catalyst, mild oxidation treatment led to decrease activity due to sintering of Pt particles. On the contrary, hydrogen treatment led to maintain activity until 5th cycle test. It was concluded from these obtained results that hydrogen treatment is suitable regeneration method during cycle test in the case of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

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